Pulse radiolysis: Pune University LINAC facility

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This note gives an account of the newly installed Pune University LINAC Facility (PULAF) for pulse radiolysis studies at the National Centre for Free Radical Research, Department of Chemistry, University of Pune. The facility consists of a 7 MeV electron accelerator coupled with optical absorption technique. The electron pulse widths can be varied from 10 ns to 3 μs with corresponding doses of about 1 to 144 Gy per pulse. The operation of both the LINAC and the detection systems is fully automated, with intersystem and safety-locking arrangements. The spectra of some important radicals measured with the PULAF are presented.

Free radicals are species containing an unpaired electron, which are unstable and react quickly with other compounds in order to capture the needed electron to gain stability. Generally, free radicals attack the nearest stable molecule, 'stealing' its electron. When the 'attacked' molecule loses its electron, it becomes a free radical itself, beginning a chain reaction. Many well-known organic reactions such as the anti-Markownikov addition, Birch reduction, and preparation of a variety of cyclic natural products involve free radicals. Many polymerization reactions also involve free radicals. In the upper atmosphere, free radicals are formed mainly due to the dissociation of chlorofluorocarbons by solar ultraviolet radiation or by reactions with other stratospheric constituents. Free radicals play an important role in a number of biological processes, some of which are necessary for life.

Study of free radical reactions: Time-resolved techniques

Free radicals are produced by several methods such as the Fenton reaction, photolysis, radiolysis, ozonation, sonolysis, etc. and their reactions studied by different techniques. The stopped-flow technique, for example, is used for following the kinetics of reactions in solution, usually in the millisecond time range, and many biologically important reactions can be investigated by this technique. The commonly used time-resolved methods for investigating the kinetics of reactive intermediates are the laser flash photolysis and pulse radiolysis techniques. This article gives a brief account of the recently established pulse radiolysis facility at the Pune University and a few of its applications in aqueous systems. A great variety of reactions can also be studied using organic solvents. However, this discussion is beyond the scope of the present article and the details can be found elsewhere[1–6].

Laser flash photolysis

The laser flash photolysis technique is used to probe reactions of reactive intermediates. With the availability of powerful lasers and extremely short pulse widths, it is now possible to probe reactions on ultrafast timescales. The biphotonic UV absorption leading to photoionization of solutes in aqueous medium has been advantageously used[7] for the study of their radical cations. The laser-driven accelerators providing electron pulses in picosecond range are in now operation in France, Japan and USA.

Pulse radiolysis

In pulse radiolysis the solution is irradiated by a short pulse of high-energy electrons generated by an accelerator to create a significant concentration of free radicals. This technique is mainly carried out using dilute aqueous solutions, where the energy is mainly spent in the production of reactive species derived from the solvent. Radiolytically generated free radicals are mostly detected using optical methods like absorption spectroscopy, resonance Raman spectroscopy, Rayleigh scattering, and also electrochemical techniques such as conductivity detection and polarography. Pulse radiolysis – ESR spectroscopy has also been used. The most commonly used detection technique, however, is absorption spectroscopy.

Water radiolysis has been the subject of a great deal of experimental and theoretical investigations. This arises from its simplicity and the wide variety of aqueous systems that are available, and partly because water systems are of special interest in radiation biology since the cell consists of a large fraction of water. For low LET radiation, water radicals contribute to cellular inactivation and cause DNA damage. Furthermore, development of nuclear reactor technology required the understanding of the mechanism of water radiolysis. Water radiolysis produces almost equal number of powerful oxidizing and reducing primary radicals.

$$H_2O \rightsquigarrow {}^{\bullet}OH\ (2.7),\ e^-_{aq}\ (2.6),\ H^{\bullet}\ (0.55),\ H_2O_2\ (0.7),\ H_2\ (0.4). \quad (1)$$

The values in the parenthesis are the G values defined as the number of molecules formed per 100 eV of energy absorbed. For chemical applications, it is usually desirable to have exclusive reducing or oxidizing conditions. This can be effectively achieved by facile manipulation of experimental conditions.

Oxidising radicals

$^{\bullet}OH$, $N_3^{\bullet}$, $SO_4^{\bullet-}$ and $X_2^{\bullet-}$ (X = Cl, Br) radicals.

The hydroxyl radical is a powerful oxidant, having a standard reduction potential of 2.7 V in acidic and 1.8 V in neutral solutions. A system containing only the $^{\bullet}OH$ radical can be obtained by purging the aqueous solution with N_2O, when the hydrated electron gets converted into the $^{\bullet}OH$ radical. The azide radical, $N_3^{\bullet}$ ($E° = 1.33$ V)[8], commonly used as a one-electron oxidant, can be produced in the system when N_2O-saturated aqueous solution containing NaN_3 is irradiated. Similarly, the sulphate radical anion, $SO_4^{\bullet-}$

($E° = 2.43$ V)[8] can be produced by the reaction of e^-_{aq} and $^•H$ with $K_2S_2O_8$. The dihalide radical anion ($X_2^{•-}$, X = Cl, Br) can be generated by adding excess of halide salt to it, so that the diradical anion is easily generated The redox potentials for $Cl_2^{•-}$, $Br_2^{•-}$ and $I_2^{•-}$ are 2.1, 1.7 and 1.1 V respectively[9]. The superoxide radical anion, $O_2^{•-}$ can be produced using the oxygenated formate solutions.

Reducing radicals

Hydrated electron and H atom. One of the early discoveries employing pulse radiolysis was the detection of hydrated electron by Hart and Boag[10,11]. Its reactions are studied in N_2-saturated aqueous solutions containing *tert*-butanol to effectively scavenge the $^•OH$ radical. The reactions of the $H^•$ atoms can be studied under acidic conditions, where the hydrated electron will be converted into $H^•$. In addition, the reducing $CO_2^{•-}$ radical can be generated from the formate ion in N_2O-saturated solutions. The interesting class of alcohol radicals can be generated using appropriate alcohol solutions. For example, the 2-hydroxy-2-propyl radicals ($E°((CH_3)_2CO)/C^•((CH_3)_2OH) = -1.8$ V) is generated by the quantitative conversion of the $^•OH$ radical under N_2O-saturated conditions containing isopropanol.

Peroxyl radicals

Peroxyl radicals play an important role in many naturally occurring processes, since almost all free radicals generated in the biological systems react rapidly with oxygen to form the corresponding peroxyl radicals. A convenient method of forming peroxyl radicals in aqueous solution is via the H-abstraction or addition to the C=C double bonds to yield substrate radicals which are converted into peroxyl radicals in the presence of oxygen[12]. Similarly, pulse radiolysis was also used to produce nitrogen oxides.

Advantages of pulse radiolysis

The pulse radiolysis method is ideal for the selective generation of radical and radical ions of interest using appropriate solution conditions, because the rate constants of a variety of reactions are well documented in the literature[3]. The precise knowledge of the radical yields makes the evaluation of kinetics easy and the rate constants and the extinction coefficients of the transients can be determined with good accuracy. Furthermore, transformation of the initially formed transients can be studied by time-resolved spectral measurements. Excited states that cannot be populated, which are forbidden by selection rules for photon interactions, can be studied.

Measurement of the spectra of the transients with low absorption coefficients is a drawback due to the poor signal-to-noise ratio. In such cases, signal averaging of several pulses needs to be done, which is time-consuming. The cost of the laser flash photolysis facility is less and it is easier to handle than the electron accelerators with accompanying costs for the building with radiation shielding and maintenance. Therefore, the pulse radiolysis equipment is usually established as a common facility for various users.

Applications of pulse radiolysis

The pulse radiolysis technique can be used to determine several properties: (a) absolute rate constants of the free-radical reactions, (b) time-resolved transient absorption spectra, (c) molar absorptivities of the transients, (d) yields of the free radicals, (e) redox potentials of radicals and (f) acid–base equilibrium constants of free-radical species. Some of its important applications have been in the synthesis of nanoparticles, experimental evidence for Marcus theory, generation of vitamin E from its radical by vitamin C, etc.

Since we can generate specific oxidizing or reducing radicals, the reduction[5,13] of metal ions by the hydrated electron in the synthesis of nanoparticles has been an important application. Miller *et al.*[14] employed pulse radiolysis to study the correlation of free energy and rates of electron transfer. Our recent work on the reactions of various alcohol radicals with a model azo dye has been correlated using the Marcus equation[15]. The generation[16] of vitamin E from its radical by vitamin C is a good example of the use of pulse radiolysis.

Redox potentials and pK_a values of the transients

Redox potentials of the transient species can be estimated by pulse radiolysis using the equilibrium between the two species using absorption measurements. The reduction potentials and absorption maxima of some selected radicals are listed in Table 1.

The pK_a values of the transient species can be measured by their interconversion by varying the pH of the solution. The inflection point of the plot of absorbance as a function of pH for the two prototropic forms gives the pK_a value of the transient.

Linear accelerator

The linear accelerator (LINAC) is an evacuated cylindrical pipe that functions as a waveguide for the accelerating field. The electrons are injected in pulses into this straight segmented waveguide (microwave cavities) and accelerated by the oscillating polarity of the electric field of an electromagnetic wave that travels down the waveguide. High-energy electrons in the range 10–20 MeV can be easily obtained using LINAC, and such high energy provides more penetrating power to the electrons and also a uniform distribution of the ionization events throughout the sample.

Pune University Linac Facility

The first pulse radiolysis facility in India was commissioned at the Bhabha Atomic Research Centre, Mumbai about two decades ago. The National Centre for Free

Table 1. Redox potential of some radicals/radical ions produced by pulse radiolysis

Radicals/radical ions	λ_{max}/nm	ε_{max} M^{-1} cm^{-1}	$E°$ (V) vs NHE
e^-_{aq}	720	18400	–2.9
$Cl_2^{•-}$	340	8800	2.1
$Br_2^{•-}$	360	9900	1.7
$N_3^•$	277	1400	1.33
$(SCN_2)^{•-}$	480	7600	1.31
$O_2^{•-}$	245	2350	–0.33
$CO_2^{•-}$	235	3000	–1.9

Radical Research (NCFRR, University of Pune, Pune) was established by the DAE–BRNS as a national facility to cater to the growing needs of researchers from the university sector, BARC and other premier national institutions. The Pune University Linac Facility (PULAF) is a 7 MeV pulsed electron accelerator and its schematic is shown in Figure 1.

The PULAF consists of a L3 (Litton) M754 grided electron gun coupled with a gun drive system designed by the American Science and Engineering (AS&E), USA. The beam from the gun is focused by a Stangeness lens coil and is then sent into the electrostatic deflector. The undeflected beam enters an S-band (2998 MHz) standing wave-guide coupled to the linear accelerator section with 17 cavities that is 80.8 cm long. This section is powered by a 26 MW (2998 MHz) magnetron with a circulator providing isolation. The pulse repetition rate is variable from 37.5 to 250 pps. The beam is confined in the accelerator section using four large Helmholtz coils that encompass the accelerator.

Figure 2 depicts the focusing Helmholtz coils and the accelerating waveguide. After the beam comes out of the accelerator, it passes through a ceramic break combined with a Bergoz FCT that provides beam-current monitoring. The end of the ceramic break contains a 0.0006″ thick Ti window that allows the electron beam to exit the vacuum system and interact with the sample. A 75 l s^{-1} Midi-Vac ion pump is connected to the accelerator and deflector to maintain vacuum for the system. Specifications of the PULAF are given in Table 2. The desired pulse widths from 10 ns to 3 μs with a selection of five pulse widths of 20, 50, 100, 200 and 400 ns are produced by an electrostatic deflector system, and pulses as short as 8 ns FWHM with peak currents of 1.1 A have been produced. Signals from the torroid for long (3 μs) and short (10 ns) pulses are plotted in Figure 3.

Detection system

The interaction of the electron beam with the matrix creates free radicals which are monitored by optical absorption using the detection system supplied by LUZCHEM, Canada. Currently, the accessible spectral range is 220–750 nm and its specifications are given in Table 3. The detection system uses a 175 W Cermax xenon lamp as a continuum source, monochromator, optical-fibre collecting system, Hamamstsu microphotomultiplier and Tektronix oscilloscope.

The kinetics and transient spectra are analysed using the Labview platform. The software enables online analysis of kinetics of formation and decay and the time-resolved absorption spectra of the transients at four different timescales using the mLFP software provided by the manufacturer. The option of signal averaging and off-line analysis of the kinetics and spectra is also available.

The safety door interlock system was developed at the NCFRR, without which the LINAC machine does not fire the pulse. The detection system was modified to suit the pulse radiolysis requirements. Both the systems are grounded separately to reduce the EMI interference. A flow system is designed for speedy absorption

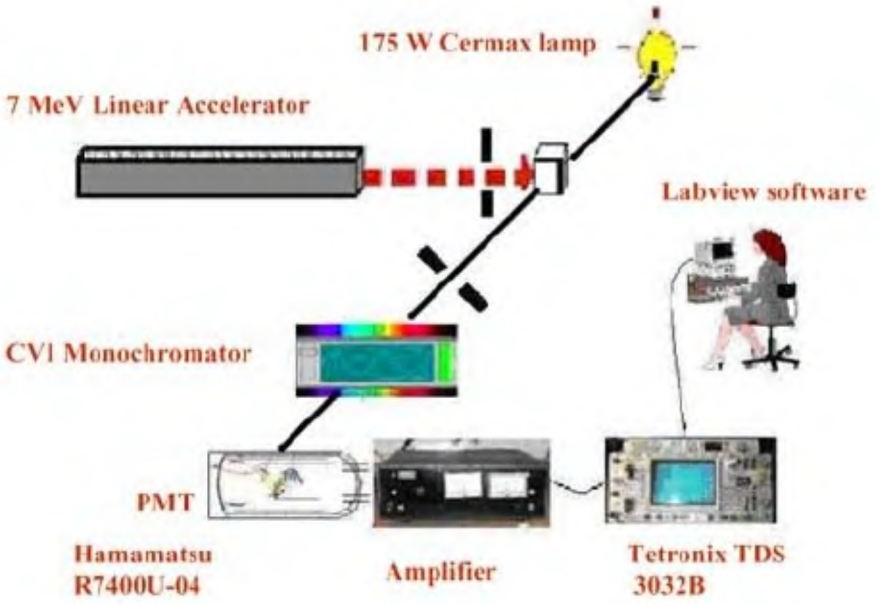

Figure 1. Schematic diagram of PULAF.

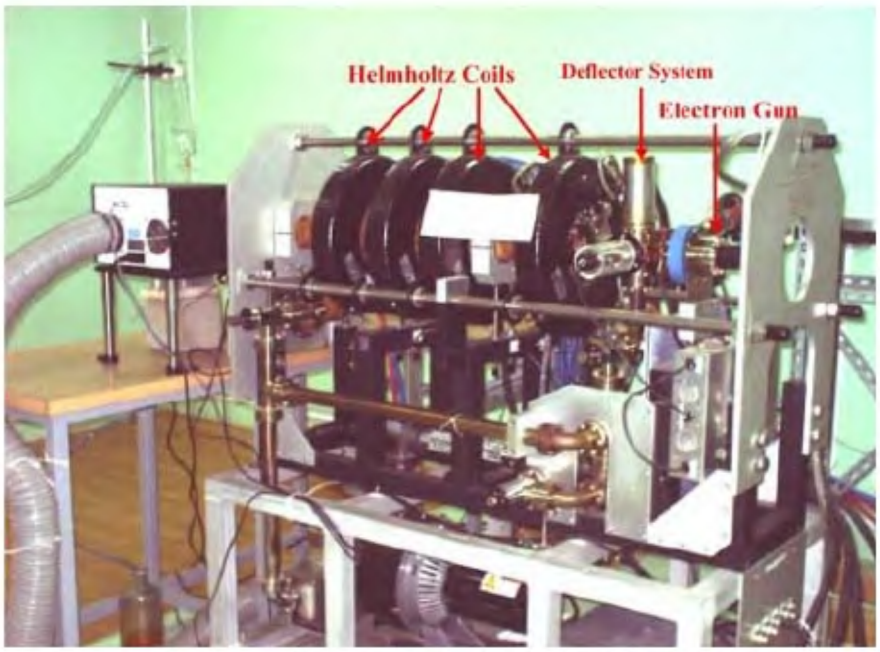

Figure 2. The 7 MeV PULAF showing Helmholtz focusing coils, waveguide consisting of 17 cavities, electron gun and deflector system.

measurements. The sample flow is regulated by a solonide valve which releases 3 ml every time a pulse is fired. About 50 ml is adequate to measure the typical spectrum from 270 to 700 nm with 10 nm interval.

Kinetics

The rate of the reaction must be sufficiently fast and the radical concentration sufficiently low (about 10^{-6} mol dm^{-3}) to avoid competing radical–radical recombination. In the study of the reactions of e^-_{aq}, its decay is monitored, whereas in the case of $H^\bullet$, $^\bullet OH$ or $O^{\bullet-}$, the growth of absorption transient formed as a result of the reaction is measured. The concentration of the reactive solute is varied to demonstrate that the pseudo first-order rate constant is proportional to the solute concentration, thus eliminating the error due to the reaction of the primary radicals with themselves or with solvent impurities.

Transient absorption spectra

After the successful installation of the PULAF last year, certain benchmark spectra were measured using the 50 ns electron pulse width to check the reproducibility and to optimize the parameters.

Thiocyanate radical anion: Aqueous solutions of N_2O-saturated KSCN (1×10^{-2} mol dm^{-3}) are commonly used as dosimeter in pulse radiolysis due to their simplicity and wide dose range. The hydroxyl radical oxidizes SCN^- ions to give the $(SCN)_2^{\bullet-}$ radical. The absorption trace (475 nm) and the spectrum of $(SCN)_2^{\bullet-}$ are shown in Figure 4, and the dose rates at different pulse widths from the reported[17] molar absorptivity values are given in Table 4.

Sulphate and bromine radical anions: The transient absorption spectra of $SO_4^{\bullet-}$ and $Br_2^{\bullet-}$ radicals (Figure 5) have been measured by PULAF. The spectrum of $SO_4^{\bullet-}$ was taken using N_2-saturated 5×10^{-2} $K_2S_2O_8$ mol dm^{-3} containing *t*-butanol (0.3 mol dm^{-3}) to scavenge the OH radical at neutral pH. The $Br_2^{\bullet-}$ radical was produced from pulse radiolysis of N_2O-saturated 5×10^{-2} KBr mol dm^{-3} solutions at pH 1. The observed maxima observed at 450 and 370 nm for $SO_4^{\bullet-}$ and $Br_2^{\bullet-}$ radicals respectively, have molar absorptivity values of 1230 and 11,000 dm^3 mol^{-1} cm^{-1}, which are in reasonable agreement with the reported[18,19] values of 1100 and 9900 dm^3 mol^{-1} cm^{-1} respectively.

Hydroxycyclohexadienyl radicals: Among organic systems, substituted benzenes are one of the most extensively studied. The $^\bullet OH$ radical has been known to react with benzenes by addition[20] to the aromatic ring forming various isomeric OH adducts. Our earlier work[21–25] has been concerned with the radiation chemical oxidation of various substituted benzenes. As an example, the time-resolved absorption spectra obtained from pulse radiolysis of N_2O-saturated solutions of 1×10^{-3} *m*-chloronitrobenzene, corresponding to its the OH adduct are shown in Figure 6.

Table 2. Specifications of PULAF

Parameter	Specification
Electron beam energy	7 ± 0.5 MeV
Peak beam current @ 10 ns	≥1 A
Peak beam current @ 3 μs	0.115 A
Beam diameter at exit window	2 ± 0.5 mm
Jitter in pulse	± 200 ps
Pulse rate	37.5 to 250 pps in 12.5 pps steps
Dose due to dark current	<1% of beam current
Pulse-to-pulse reproducibility	±1%
Energy spread	±0.5 MeV
Exit window material	Titanium
Modes of operation	
Single shot	
Multi-shots	37.5 to 250 pps
Preset beam pulses	10 to 250 pulses in steps of 10 pulses
Pulse width	10, 20, 50, 100, 200, 400 ns and 3 μs
Pre-trigger delay	10 μs, 100 μs, 1 ms
Sequential delay generator	Delay for shutter and oscilloscope

Table 3. Specifications of the detection system

Lamp	Cermax 175 W parallel lamp (spectral range 200–1600 nm)
Monochromator	CVI 110 mm, ruled gratings, 1200 lines/mm (Spectral range 200–750 nm)
PMT	Hamamatsu R-7400U - 04 (spectral range 185–850 nm)
	Rise time: 0.78 ns
PMT Power supply	Programmable, –1000 V
Digitizer	TDS 3032B
	Bandwidth: 300 MHz, sampling rate 2.5 Gs/s
Software	Supplied as an executable code in the form of compiled Lab-VIEW application. The spectrometer software allows for full computer-controlled data acquisition with PMT, including single shot and multi-shot kinetics, time-resolved spectra. Off-line analysis software allows extraction of kinetic and spectral information.

Areas of research

The PULAF is being used by several researchers from the University of Pune, BARC and other universities and institutes. The areas pursued by some of the researchers are briefly described here.

Table 4. Dose rates at different pulse widths from reported molar absorptivity values[17]

Pulse width/ns	Dose per pulse/Gy
10	~1
20	4
50	17
100	38
200	52
400	56
3000	144

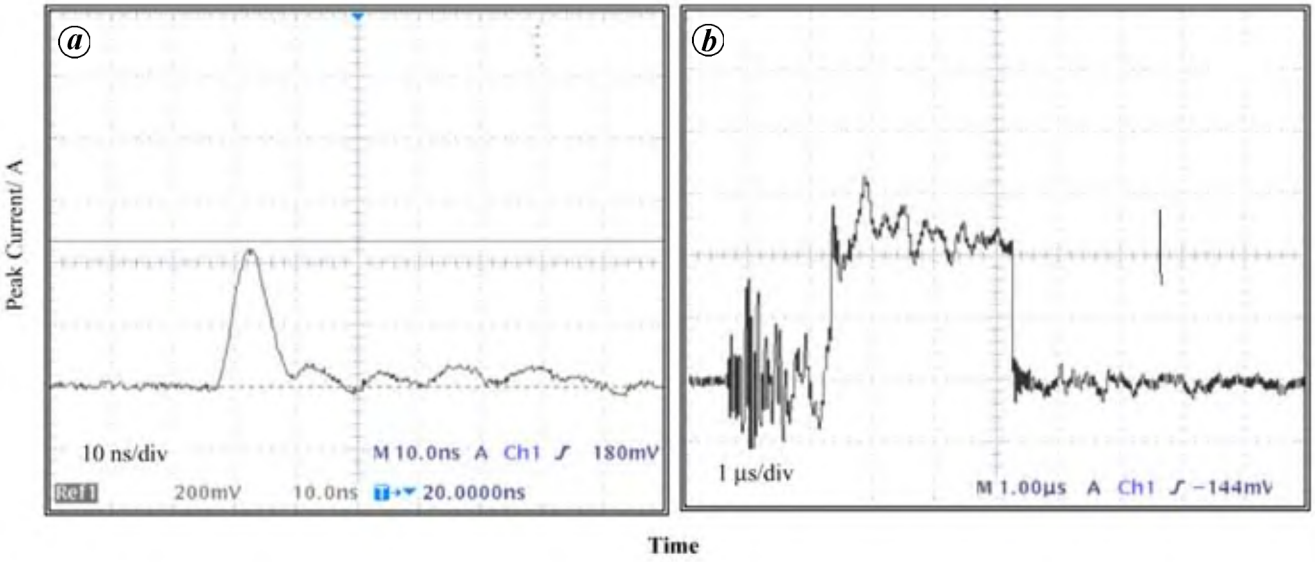

Figure 3. Torroid output for 10 ns (***a***) and 3 µs (***b***) electron-beam pulses.

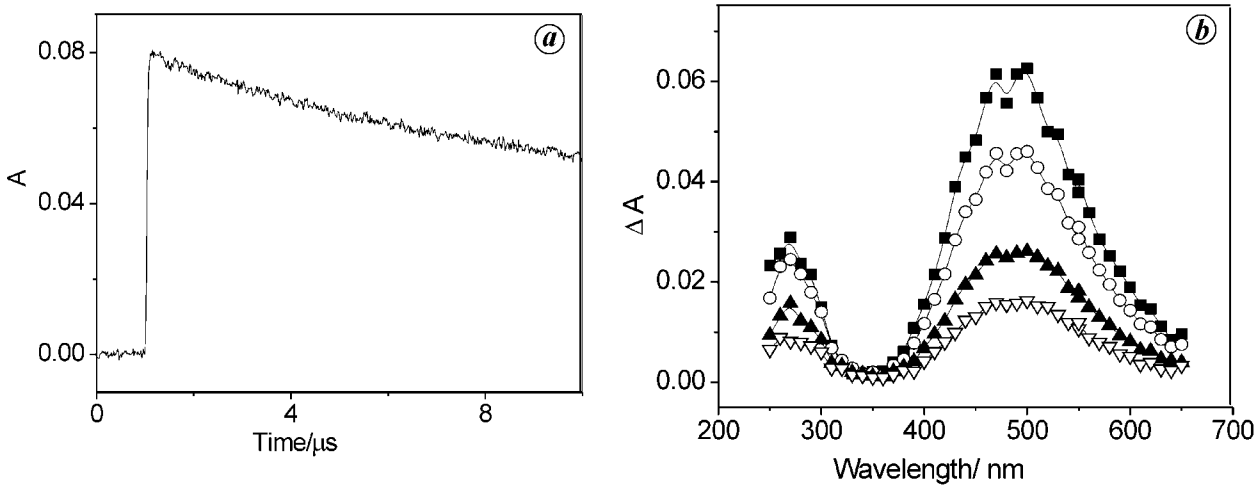

Figure 4. ***a***, Decay trace of $(SCN)_2^{\bullet-}$. ***b***, Time-resolved absorption spectra of $(SCN)_2^{\bullet-}$ at (■) 0.5, (○) 10, (▲) 40 and (▽) 80 µs after the pulse; [solute] = N_2O saturated KSCN (1×10^{-2} mol dm^{-3}) solutions at neutral pH. Dose/pulse = 14 Gy.

Antioxidants

The BARC group has initiated work on a class of antioxidants, which include amino acids such as tryptophan and its derivatives. Another research project by the Pune University zoology group has been concerned with the evaluation of the antioxidant activity of an herbal antidiabetic drug extract to determine the $ABTS^{\bullet-}$ and $CO_3^{\bullet-}$ radical scavenging capacity[26,27].

Inorganic complexes

The rate constants and the spectra of the transients following the reactions of oxidizing and reducing radicals with polypridyl ligands and their complexes with Ru and Cu are measured, and further work with other complexes is under way.

Organic sulphur compounds

Free radicals and radical ions derived from sulphur-containing compounds have been widely studied. Recently, it has been shown[28] by us that oxidation in methonine methyl ester occurs at the sulphur site. On the other hand, in aryl-substituted sulphur compounds, the benzene ring acts as an additional site for the radical attack, and the study on oxidation of N-carbobenzyloxy methionine has been carried out using the PULAF.

Cinnamic acid derivatives

Cinnamic acid/cinnamate and its derivatives form an interesting class of compounds to examine the reactivity of the $^{\bullet}OH$ radical attack on the ring and the substituent. The work carried out at the BARC pulse radilysis facility has been extended to the study of reactions of both oxidizing ($^{\bullet}OH$, $O^{\bullet-}$, $N_3^{\bullet}$ and $SO_4^{\bullet-}$) and reducing ($^{\bullet}H$ and e_{aq}^-) radicals with a large number of cinnamic acid derivatives containing –OH, $–OCH_3$, –Cl or $–NO_2$.

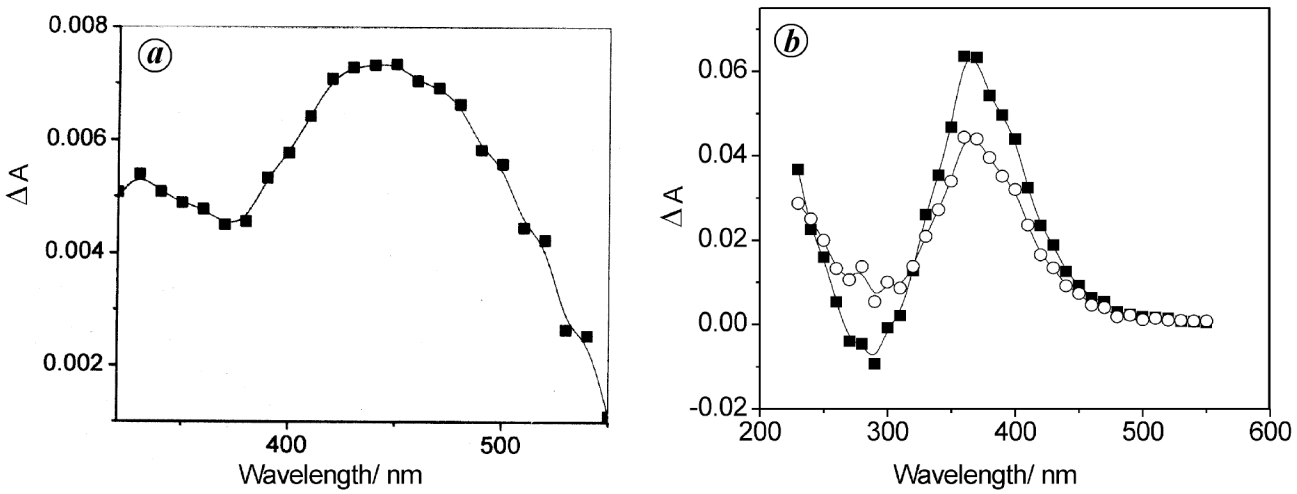

Figure 5. ***a***, Absorption spectrum of $SO_4^{\bullet-}$ at 0.5 μs after the pulse; [solute] = N_2 saturated 5×10^{-2} $K_2S_2O_8$ mol dm^{-3} containing *t*-butanol (0.3 mol dm^{-3}) to scavenge OH radical at neutral pH. Dose/pulse = 18 Gy. ***b***, Time-resolved absorption spectra of $Br_2^{\bullet-}$ at pH 1 (■) 0.5 and (○) 10 μs after the pulse. Dose/pulse = 10 Gy; [solute] = 5×10^{-2} mol dm^{-3}.

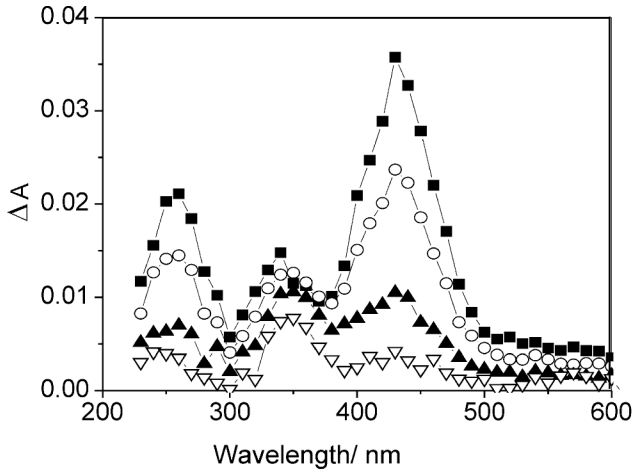

Figure 6. Time-resolved absorption spectra recorded in the reaction of OH radical with *m*-chloronitrobenzene (■) 2.5, (○) 40, (▲) 200 and (▽) 850 μs after the pulse; [solute] = N_2O saturated solutions of 1×10^{-3} *m*-chloronitrobenzene at neutral pH. Dose/pulse = 14 Gy.

Derivatives of nucleobases

Recently, the MG University group carried out detailed investigation[29] of the reactions of $^{\bullet}OH$ radical with pyrimidine derivatives, 5-azacytosine and 5-azacytidine in aqueous medium using the PULAF.

Researchers desirous of availing the PULAF can contact, along with a brief research proposal, Dr Avinash Kumbhar, Project Coordinator, NCFRR, Department of Chemistry, University of Pune, Pune 411 007, India. e-mail: askum@chem.unipune.ernet.in. Telephone: 020-25601371/25690618, Mobile: 09890607871, Fax: 020-25691728.

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